

# Effect of Interparticle Interactions on the Rate of Injection of Charge Carriers into Electroactive Polymer Films\*

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**Abstract**—A phenomenological approach is used for deriving a difference equation for the density of reduced sites in films of electroactive polymers with conspicuous interparticle interactions. The approach involves simultaneous application of the lattice methods and Broensted's rule. This leads to generalization of equations for the surface layer that are known in theory of surface tension for nonelectrolytic solutions. Together with the Poisson equation for electric potential, the derived relationships make a complicated system of differential equations. Nevertheless, it can be solved by iterative methods. In the framework of this approach, expressions for the rates of injection of charge carriers into polymer films are obtained. Within a first approximation with regard to allowance for the forces of short-range interactions, their influence on the rates of injection of electrons and protons into a film is discussed.

*Key words:* electroactive polymer, film, injection, charge carrier, interparticle interaction, model

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## I. INTRODUCTION

Substantial progress achieved in research on the regularities governing the charge transport in modified electrodes is largely connected with use of spectroscopy of the electrochemical impedance. However, the interpretation of data on the impedance of modified electrodes is frequently ambiguous, because of the many-parameteredness of the description of transport in these objects. For example, in the most developed model for a uniform electroactive film with two sorts of charge carriers, a correct description of the process of charging the electric double layers (EDL) on its boundaries requires that four parameters be introduced for each side of the film [1, 2]. Apart from the commonly used parameters, i.e. the resistance to charge transfer and the double-layer capacitance, a theory also features a double-layer number and an asymmetry factor. All these parameters are phenomenological, for their introduction was usually realized at the expense of the application of Gibbs' adsorption equation [1, 2]. A model approach that was by the authors of this particular communication in [3] allows the authors of this particular communication to establish, at the very least in a numerical form, dependences of the said parameters on the electrode potential and the concentration of the washing electrolyte. Calculation of these dependences

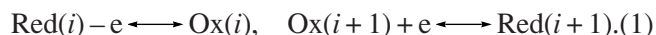
and their subsequent comparison with data obtained experimentally would allow us to reduce the number of parameters required for a description of the impedance of a modified electrode and thus alleviate the interpretation of corresponding results. It is necessary to underline at this particular juncture that in [3], apart from the assumption about a uniform nature of films there was used the assumption about the inessentialness of interparticle interactions in the bulk of a polymer film, i.e. about the inconsiderableness of the so-called effect of the short-range interaction. Although the fundamental aspects pertaining to the effect of such interactions on the kinetics of the charge transfer processes in the bulk of films are transparent enough, their introduction in the course of the description of the injection kinetics of charge carriers into a film happens to be nontrivial. To make this statement transparent and to explain the model that would simultaneously be used in what follows for the description of a polymer film, it would help to consider a particular technique used for taking into account the so-called effect of the short-range interaction, which was performed previously in work [4].

## II. THE MODEL

In this work a polymer film was likened to an ideal cubic lattice at the points of which reduced (Red) and oxidized (Ox) fragments of something were deployed, which provided for the electron transfer between neigh-

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boring points of the lattice in accordance with the reaction



For the rate of transfer  $j(i)$  of electrons out of the  $i$ th and into the  $i+1$ th plane of such a lattice there was used the following equation:

$$j(i) = k_0 \{ \exp[-E_s/RT] C_R(i) [1 - \theta_R(i+1)] - \exp[-E_r/RT] C_R(i+1) [1 - \theta_R(i)] \}. \quad (2)$$

Here,  $k_0$  the preexponential factor of constants of rates of transfer of electrons;  $E_s$  and  $E_r$  are activation energies in the direct and reverse directions of transfer, respectively;  $\theta_R(j) = C_R(j)/C$  is the coverage of the  $i$ th plane of the lattice by the reduced form (count  $0 \leq i \leq M$  is taken from a substrate so that the value  $i = 0$  corresponds to the surface of the latter,  $M$  is the overall number of layers in the lattice); and  $c$  is the summed up and independent of the number  $i$  concentration of the oxidized and reduced forms. As reactions (1) that describe the transfer between different planes  $i$  are similar (with the exception of  $i = 0, M$  and, strictly speaking,  $i = 1, M - 1$ ), for activation energies we can write the Broensted rule

$$\begin{aligned} E_s(i) &= E_0 - \alpha \Delta Q(i, i+1); \\ E_r(i) &= E_0 + \beta \Delta Q(i, i+1); \quad \alpha + \beta = 1, \end{aligned} \quad (3)$$

where  $\Delta Q(i, i+1)$  is a generalized heat effect of reaction (1) that includes variations in the electrostatic constituent of energy (as calculated per mole of every reacting species):

$$\begin{aligned} \Delta Q(i, i+1) &= W_R(i) + W_{\text{Ox}}(i+1) - W_R(i+1) \\ &- W_{\text{Ox}}(i) + (z_0 - 1)F\varphi(i) + z_0F\varphi(i+1) \\ &- (z_0 - 1)F\varphi(i+1) - z_0F\varphi(i). \end{aligned} \quad (4)$$

Here,  $\varphi(i)$  is the electric potential of the  $i$ th plane of the lattice (relative to the thickness of the solution washing the film) and  $z_0$  is the charge of the oxidized species, so that  $z_0 - 1$  is the charge of the reduced species. The non-electrostatic constituents of energy  $W_R(i)$  and  $W_{\text{Ox}}(i)$  of relevant species were calculated in the framework of the Bragg–Williams approximation (or, which is the same, “molecular field”), which, omitting intermediate manipulations, was leading to following expression for the heat effect:

$$\begin{aligned} \Delta Q(i, i+1) &= \{ W_R^0(i) + W_{\text{Ox}}^0(i+1) - W_R^0(i+1) \\ &- W_{\text{Ox}}^0(i) \} + F[\varphi(i+1) - \varphi(i)] \\ &- 4\Delta E[\theta_R(i+1) - \theta_R(i)] - \Delta E[\theta_R(i+2) - \theta_R(i-1)] \\ &+ \Delta E[\theta_R(i+1) - \theta_R(i)], \end{aligned} \quad (5)$$

where  $\Delta E = \varepsilon_{\text{RR}} + \varepsilon_{00} - 2\varepsilon_{\text{R0}}$  is the so-called parameter of Flori, i.e. the sum of energies of paired interactions between species of the same type minus twice the energy of interaction between species of different types with one another. As the lattice was presumed to be uni-

form, then, to within an accuracy of the deformational constituents of energy, which are ignored here, we deem it possible to presume that the addends in the braces mutually counterbalance one another and it may be dropped. Nevertheless, it would make sense to preserve it, in order to always remember about its other-than-zero value in the case where  $i = 1, M - 1$  and, the more so, at  $i = 0, M$  in similar expressions for the heat effect of corresponding transfer stages (see further on).

No explanation is required for the physical meaning of the second addend in the right-hand part of (5). The third addend apparently corresponds to the difference between energies of interaction of the reacting species with the nearest environment surrounding them in the planes  $i+1$  and  $i$ , whereas the fourth addend corresponds to the difference in the interactions of species with the layers of the cubic lattice adjacent to them ( $i+2$ nd and  $i-1$ st for planes  $i+1$  and  $i$ , respectively). The last addend in the right-hand part of (5) arises because of the occurring in the course of reaction (1) change in the localization of reacting species, which counterbalances in part the effect of the third addend in the right-hand part of the same relationship.

Further on, the difference of the difference  $[\theta_R(i+2) - \theta_R(i-1)]$  from the triple difference  $[\theta_R(i+1) - \theta_R(i)] = \Delta\theta_R(i)$  in work [4] was ignored, which in the final analysis led to the equation

$$\begin{aligned} j(i) &= -k_0 \exp[-E_0/RT] \{ \Delta C_R(i) \\ &- C_R(i) [1 - \theta_R(i)] [(F/RT)\Delta\varphi(i) - a_0\Delta\theta_R(i)] \} \end{aligned} \quad (6)$$

which was linearized with respect to increments, or, in the framework of a continuous description, to the equation

$$\begin{aligned} j(z) &= -\lambda k_0 \exp[-E_0/RT] \{ dC_R(z)/dz \\ &- C_R(z) [1 - \theta_R(z)] d[F\varphi(z)/RT - a_0\theta_R(z)]/dz \}, \end{aligned} \quad (7)$$

where  $\lambda$  denotes the lattice constant;  $a_0 = 6\Delta E/RT$  represents a dimensionless attraction constant (in the general case, the coordination number of the lattice is equal to  $c$ , and then  $a_0 = c\Delta E/RT$ ); and  $z$  is a distance from the substrate.

It is necessary to underline at this juncture that, following the substitution of the diffusion coefficient of electrons  $D_e$  for the factor  $\lambda k_0 \exp[-E_0/RT]$ , equation (7) will completely coincide with the equation that describes the electron transfer and which was adopted in models of heterogeneous films of electroactive polymers (see for example [5, 6]). And this circumstance does not seem to be surprising, because, as was already mentioned in [4], both in its final content and in the meaning of transformations that were conducted in the course of its derivation, equation (7) corresponds to the proportionality of an electron flux to the gradient of the electrochemical potential of the electrons in the film, i.e. to the initial assumption underlying thermodynamics of irreversible processes. At the same time, it is clearly distinguishable, from the brief description of the approach to an allowance for the effect of the short-

range interaction that was used in [4], that, apart from the assumptions that were connected with the application of a simplistic model for the polymer lattice, when deriving equation (6) (and, later on, equation (7)), there were introduced still additional assumptions. These additional assumptions, as we have already mentioned in the foregoing, are the assumptions concerning the inessentialness of the elastic constituents of the energy of species and the assumptions concerning the possibility of representation of the difference  $[\theta_R(i+2) - \theta_R(i-1)]$  in the form of the tripled difference  $[\theta_R(i+1) - \theta_R(i)]$ . Finally, it should also be pointed out that, even if all these assumptions have been valid, the difference equation (6) would have to alter its shape for values  $i = 1, M - 1$ , i.e. for the planes of the lattice that are adjacent to the substrate and the solution, respectively. The necessity to take into account these circumstances, the more so the last one, as a circumstance directly affecting the conditions of the charge injection into a film, seems to be obvious. In connection with this and to continue with the analysis that was begun in [3], in this particular communication we offer particular solution for at least some of the raised questions, which will be being realized in the framework of the approach that was used in [4].

### III. RESULTS

Complementing an analysis of work [4], we will take into account the fact that the difference between the coverages  $[\theta_R(i+2) - \theta_R(i-1)]$  that appears in (5) is represented in the general case in the form

$$[\theta_R(i+2) - \theta_R(i-1)] = 3[\theta_R(i+1) - \theta_R(i)] + \{[\theta_R(i+2) - 2\theta_R(i+1) + \theta_R(i)] - [\theta_R(i+1) - 2\theta_R(i) + \theta_R(i-1)]\} = 3\Delta\theta_R(i) + \Delta^3\theta_R(i)$$

where  $\Delta\theta_R(i)$  and  $\Delta^3\theta_R(i)$  are the first and third differences with respect to  $\theta_R(i)$ . In the general case, therefore, (6) should be written down in the form

$$j(i) = -k_0 \exp[-E_0/RT] \{ \Delta C_R(i) - C_R(i)[1 - \theta_R(i)][(F/RT)\Delta\varphi(i) - a_0\Delta\theta_R(i) - (a_0/c)\Delta^3\theta_R(i)] \}, \quad (6a)$$

and instead of (7),

$$j(z) = -\lambda k_0 \exp[-E_0/RT] \{ dC_R(z)/dz - C_R(z)[1 - \theta_R(z)]d[F\varphi(z)/RT - a_0\theta_R(z)] - (\lambda^2 a_0/c)d^2\theta_R(z)/dz^2 \}. \quad (7a)$$

In the case of equilibrium equations (6a) after preliminary division by  $C_R(i)[1 - \theta_R(i)]/RT$  may be summed from  $i = 2$  to any arbitrary  $i < M-1$ , which gives

$$(RTa_0/c)\Delta^2\theta_R(i) + RT \ln\{\theta_R(i)/[1 - \theta_R(i)]\} + RTa_0\theta_R(i) - F\varphi(i) = \tilde{\mu}_e(f) - \mu_e^0(f), \quad (8)$$

where  $\tilde{\mu}_e(f)$  is the electrochemical potential of electrons in a film and  $\mu_e^0(f)$  is the standard chemical potential of electrons in the same film. An analogue of (8) in the case of a continuous description, obviously, is

$$(RT\lambda^2 a_0/c)d^2\theta_R(z)/dz^2 + RT \ln\{\theta_R(z)/[1 - \theta_R(z)]\} + RTa_0\theta_R(z) - F\varphi(z) = \tilde{\mu}_e(f) - \mu_e^0(f). \quad (9)$$

Commenting on equations (8) and (9), it should be noted that their analogues for the case of non-electrolytes have long since been known (on the order of 50 years). These are the so-called equations of the surface layer, which were obtained in the framework of the lattice methods by Ono [7] and, somewhat later, when the continuous approach was used by Cahn and Hilliard [8] (see also works [9, 10] concerning simulation of the cytoskeleton of nerve fibers). The advantage of these equations (as compared with equations that contain no addends with a 2nd difference or a 2nd derivative) is that the equations in question offer one a chance to describe the following interfaces: liquid/gas and two immiscible liquids, for one equation ((8) or (9)) ensures the presence of two different bulk values of  $\theta_R$  and a transitional region in between them. It is also obvious that with the aid of these equations one can simulate a solid body/liquid interface. A certain impediment for such a generalization seems to be that, in contradistinction to the interfaces: liquid/liquid and liquid/gas, equation (8) (and, therefore, equation (9) as well) is invalid for  $i = 0, 1, M-1, M$ , as we have already mentioned in the foregoing and as it must be obvious from what we stated above. Below we will show that, should some certain conditions be fulfilled, this impediment may be removed.

#### 1. Generalization of Previous Results

To obtain generalized results we will turn our attention to the cases of values of  $i$  for which the results that were obtained in the foregoing are not quite correct. In the first place, we will perform the corresponding consideration for  $i = 1, M-1$ . To perform this consideration, we will use the same scheme that was used previously. In particular, for the rate of transfer  $j(1)$  from the first layer into the second layer (i.e.  $i = 1$ ), we will, as previously, employ equation (2) complemented by the Broensted rule (3). A calculation of the heat effect for this particular stage of the transfer process, which is similar to a calculation that had been performed previously, yields

$$\Delta Q(1, 2) = W_R^0(1) + W_{Ox}^0(2) - W_R^0(2) - W_{Ox}^0(1) + \varepsilon_{RM} + \varepsilon_{00} - \varepsilon_{R0} - \varepsilon_{0M} - \Delta E \theta_R(\mathbf{0}) - \Delta E [\theta_R(3) - \theta_R(\mathbf{0})] + \Delta E \Delta \theta_R(1) - 4\Delta E \Delta \theta_R(1) + F[\varphi(2) - \varphi(1)]. \quad (10)$$

The fresh parameters that appear in the last equation are  $\epsilon_{RM}$  and  $\epsilon_{0M}$ , which are the energies of the interaction of the reduced and oxidized forms (calculated per mole of these species) with the surface of the substrate. As far as the addends that are singled out with bold print are concerned, these cancel out one another, but these are nevertheless introduced on purpose, in order for the expression obtained for  $\Delta Q(1, 2)$  to have a form that would be identical to the form of  $\Delta Q(i, i + 1)$  with  $1 < i < M-1$ , that were calculated previously. To attain this, let us determine the “imaginable” coverage of the surface of the substrate  $\theta_R(0)$  with the aid of the relationship

$$\theta_R(0) = \{ W_R^0(1) + W_{Ox}^0(2) - W_R^0(2) - W_{Ox}^0(1) + \epsilon_{RM} + \epsilon_{00} - \epsilon_{R0} - \epsilon_{0M} \} / \Delta E. \quad (11)$$

Without paying so far any attention to the introduced definition, we deem it possible to point out that it gives us a chance to employ equations (6) and (6a) now for the value  $i = 1$ .

We can use the same device in order to generalize equations (6) and (6a) to the case where  $i = M-1$ . The resultant expression for  $\Delta Q(M-1, M)$  in so doing will have the following form:

$$\begin{aligned} \Delta Q(M-1, M) &= W_R^0(M-1) + W_{Ox}^0(M) \\ &- W_R^0(M) - W_{Ox}^0(M-1) + \epsilon_{0S} - \epsilon_{00} + \epsilon_{R0} - \epsilon_{RS} \\ &+ \Delta E \theta_R(M+1) - \Delta E [\theta_R(M+1) - \theta_R(M-2)] \\ &+ \Delta E \Delta \theta_R(M) - 4 \Delta E \Delta \theta_R(M) + F[\varphi(M) - \varphi(M-1)]. \end{aligned} \quad (10a)$$

Here,  $\epsilon_{0S}$  and  $\epsilon_{RS}$  are the energies of the interaction of the oxidized and reduced quasi-species with the solution and the “imaginable” coverage  $\theta_R(M+1)$  will be determined with the aid of the relationship

$$\theta_R(M+1) = -\{ W_R^0(M-1) + W_{Ox}^0(M) - W_R^0(M) - W_{Ox}^0(M-1) + \epsilon_{0S} - \epsilon_{00} + \epsilon_{R0} - \epsilon_{RS} \} / \Delta E. \quad (11a)$$

With the said definitions, equations (6) and (6a) happen to be valid for all  $i$  from the interval  $[0, M]$  and, correspondingly, equations (7) and (7a), for all  $z$  out of the interval  $[0, L]$ , where  $L$  is the thickness of a film. Before embarking on a discussion concerning the restriction intrinsic to the performed generalization, one should look up what the device we used offers for the rate of injection of electrons into a film  $j(0)$ , i.e. in the case of the plane  $i = 0$ .

## 2. The Rate of Injection of Electrons from the Substrate into the Film

For the injection of rate we will use the equation

$$\begin{aligned} j(0) &= \sigma_e \exp[-E_s(0)/RT][1 - \theta_R(1)] \\ &- \rho_e \exp[-E_r(0)/RT]\theta_R(1), \end{aligned} \quad (12)$$

where the preexponential factors  $\sigma_e$  and  $\rho_e$  are now not equal to one another as was assumed previously. Nevertheless, we will employ the Broensted rule in the previous form:

$$\begin{aligned} E_s(0) &= E_{01} - \alpha_1 \Delta Q(0, 1); \\ E_r(0) &= E_{01} + \beta_1 \Delta Q(0, 1); \quad \alpha_1 + \beta_1 = 1. \end{aligned} \quad (13)$$

This form differs from (3) only at the expense of the introduction of an additional subscript. A calculation of the heat effect  $\Delta Q(0, 1)$  in the same approximation that was used previously gives

$$\begin{aligned} \Delta Q(0, 1) &= \mu_e^0(\text{Me}) + W_{Ox}^0(1) - W_R^0(1) \\ &+ \epsilon_{0M} + \epsilon_{00} - \epsilon_{RM} - \epsilon_{R0} + 4(\epsilon_{00} - \epsilon_{R0}) \\ &+ F[\varphi(1) - E] - \Delta E \theta_R(2) - 4 \Delta E \theta_R(1), \end{aligned} \quad (14)$$

where  $E$  is the potential of the electrode (substrate surface) and  $\mu_e^0(\text{Me})$  is the standard chemical potential of electrons in the substrate. We can again transform this result in an identical manner by introducing  $\theta_R(0)$ , which would allow us to rewrite (14) in the following form:

$$\begin{aligned} \Delta Q(0, 1) &= \mu_e^0(\text{Me}) + W_{Ox}^0(1) - W_R^0(1) \\ &+ \epsilon_{0M} + \epsilon_{00} - \epsilon_{RM} - \epsilon_{R0} + 4(\epsilon_{00} - \epsilon_{R0}) \\ &+ F[\varphi(1) - E] + \Delta E \theta_R(0) - \Delta E [\theta_R(2) - 2\theta_R(1) \\ &+ \theta_R(0)] - 6 \Delta E \theta_R(1). \end{aligned} \quad (14a)$$

With the previously determined expression for  $\theta_R(0)$ , specifically,  $\theta_R(0) = \{ W_R^0(1) + W_{Ox}^0(2) - W_R^0(2) - W_{Ox}^0(1) + \epsilon_{RM} + \epsilon_{00} - \epsilon_{R0} - \epsilon_{0M} \} / \Delta E$ , taken into account, it follows from (14a) that

$$\begin{aligned} \Delta Q(0, 1) &= \mu_e^0(\text{Me}) + 4(\epsilon_{00} - \epsilon_{R0}) + W_{Ox}^0(2) \\ &- W_R^0(2) - (\epsilon_{R0} - \epsilon_{00}) - 6 \Delta E \theta_R(1) \\ &- \Delta E \Delta^2 \theta_R(1) + F[\varphi(1) - E], \end{aligned} \quad (14b)$$

where  $\Delta^2 \theta_R(1) = [\theta_R(2) - 2\theta_R(1) + \theta_R(0)]$  is formally the second difference with respect to  $\theta_R(i)$  for the plane  $i = 1$ . However, the second difference  $\Delta^2 \theta_R(1)$  is defined by equation (8) for  $i = 1$ , which is in essence the integral (6a) in the case of equilibrium. Indeed, we have demonstrated in the foregoing that (6a) (and, consequently, (8), as well) is valid at  $i = 1$  at some restrictions that are thus far unknown. Consequently, presuming that the injection of stage if the limiting stage and all the subsequent stages are equilibrium, we can use (8) in order to



determine  $\Delta^2\theta_R(1)$ . This in the final analysis allows us to write down the following expression for injection of:

$$j(0) = [\theta_R(1)]^{\alpha_1} [1 - \theta_R(1)]^{\beta_1} \{ \sigma'_e [(1 - \theta_R^0)/\theta_R^0]^{\alpha_1} \times \exp[-\alpha_1 a_0 \theta_R^0] \exp[-(\alpha_1 F/RT)(E - \varphi^0)] - \rho'_e [\theta_R^0/(1 - \theta_R^0)]^{\beta_1} \exp[\beta_1 a_0 \theta_R^0] \times \exp[(\beta_1 F/RT)(E - \varphi^0)] \}. \quad (15)$$

The constants  $\sigma'_e$ , and  $\rho'_e$  in the last expression differ from  $\sigma_e$  and  $\rho_e$  by some constant factors, which take into account both the activation energy  $E_{01}$  and the following sum of the constituents of the heat effect  $\{ \mu_e^0(\text{Me}) + 5(\varepsilon_{00} - \varepsilon_{R0}) + W_{\text{Ox}}^0(2) - W_{\text{R}}^0(2) \}$ :

$$\begin{aligned} \sigma'_e &= \sigma_e \exp \{ -E_{01}/RT + \alpha_1 [\mu_e^0(\text{Me}) + 5(\varepsilon_{00} - \varepsilon_{R0}) + W_{\text{Ox}}^0(2) - W_{\text{R}}^0(2)]/RT \}; \\ \rho'_e &= \rho_e \exp \{ -E_{01}/RT - \beta_1 [\mu_e^0(\text{Me}) + 5(\varepsilon_{00} - \varepsilon_{R0}) + W_{\text{Ox}}^0(2) - W_{\text{R}}^0(2)]/RT \}; \end{aligned}$$

and  $\theta_R^0$  and  $\varphi^0$  are the occupations of the lattice by the reduced form in the bulk of the film.

Paying no attention at this juncture to the restrictions concomitant to the description we use, let us state that this approach seems to us to be on the whole correct. The grounds for such a statement include not only the generalization, in the framework of the developed approach, of the earlier-known equations for the surface layer, but also the circumstance that the relationships, which were obtained in the course of derivations, are very luckily transformed. For example, the coverages  $\theta_R(0)$  and  $\theta_R(M + 1)$  that were introduced in the foregoing on the basis of formal considerations fit the subsequent description in a natural fashion. In particular, the definition of the first of these "works" in the expression for the injection rate, leading to the appearance, in the heat effect of this process, of the 2nd difference  $\Delta^2\theta_R(1)$ , which is given, for equilibrium conditions of transfer in subsequent layers of the lattice, by the obtained condition of the constancy of the electrochemical potential of electrons in any arbitrary layer of the film. We deem it possible to presume with assurance that, should it have been necessary to determine the rate of injection of electrons into solution (i.e.  $j(M)$ ), the entire chain of lucky transformations performed in the foregoing would fully have repeated itself. All this speaks of intrinsic consistency of the developed description. Speaking now of its limitations, it should be noted that, in the framework of the simplistic model we used, the limitation of the approach under discussion as a whole is, obviously, the smallness, by the absolute value, of the ratio of  $\Delta E \Delta \theta_R(i)/RT$  for the val-

ues  $i \neq 0, 1, M-1, M$ . If this constraint is complemented by the requirement that the coverages  $\theta_R(0)$  and  $\theta_R(M + 1)$  that were determined in the foregoing be not too far removed from the values in the interval (0, 1), then the linearization of  $\exp(\pm \Delta E \Delta^3 \theta_R(i)/RT)$  (where  $i$  now includes values  $i = 1, M$ ), which is performed in the course of subsequent transformations, would be correct, i.e. the developed procedure is on the whole justified. It follows that, by their character, the restrictions that arise with respect to the coverages  $\theta_R(0)$  and  $\theta_R(M + 1)$  are consistent with the said overall limitation of the approach and, in connection with this, do not seem excessively hard.

Passing now to a preliminary discussion of the consequences resulting from the description that was presented in the foregoing and not dwelling upon other aspects of its application apart from the application to electroactive films, it should be pointed out that the starting point for such an application is equation (15). According to it, in order to write down the injection rate in an explicit form, it is necessary to know the occupation of the first layer of the lattice  $\theta_R(1)$  or a near-surface occupation in the case of the use made of a continuous description, which is precisely the description we are going to employ further on. One can find this degree of occupation by solving equation (9). Sadly enough, in the general case, only numerical solution of this equation is feasible. However, the first integral of a system that comprises this equation, analogous-to-it condition of constancy of the electrochemical potential of counterions, and the Poisson equation, is possible to find.

### 3. The First Integral of an Equilibrium System of Equations for the Surface Layers in Films of Electroactive Polymers with Two Sorts of Charge Carriers

The system of equations in question has the following form:

$$\begin{aligned} (RT\lambda^2 a_0/c) d^2\theta_R(z)/dz^2 + RT \ln \{ \theta_R(z)/[1 - \theta_R(z)] \} \\ + RT a_0 \theta_R(z) - F\varphi(z) = \tilde{\mu}_e(f) - \mu_e^0(f), \\ RT \ln c_m(z) + z_m F\varphi(z) = \tilde{\mu}_m(f) - \mu_m^0(f), \quad (16) \end{aligned}$$

$$d^2\varphi(z)/dz^2 = -(4\pi F/\varepsilon_f) [z_0 C + z_m C_m(z) - c_R(z)],$$

where  $\tilde{\mu}_m(f)$  and  $\mu_m^0(f)$  are the electrochemical and the standard chemical potentials of counterions in the film;  $C_m(z)$  and  $z_m$  are their concentration in the film and chargeness, respectively; and  $\varepsilon_f$  is the dielectric constant of the film. Multiplying the first equation of system (16) by  $[dC_R(z)/dz]dz$  and the second equation of system (16) by  $[dC_m(z)/dz]dz$  and then taking the sum

of the results thus obtained with simultaneous allowance for the third equation of system (16), we obtain

$$\begin{aligned} & [(RT\lambda^2 a_0/Cc)d^2 C_R(z)/dz^2 \\ & + RT\ln\{\theta_R(z)/[1-\theta_R(z)]\} + (RTa_0/C)C_R(z)] \\ & \times [dC_R(z)/dz]dz + [RT\ln C_m(z)]dC_m(z) \\ & - (\varepsilon_f/4\pi)\varphi(z)[d^3\varphi(z)/dz^3]dz \\ & = [\tilde{\mu}_e(f) - \mu_e^0(f)]dC_R(z) + [\tilde{\mu}_m(f) - \mu_m^0(f)]dC_m(z). \end{aligned} \quad (17)$$

As seen, both parts of this equation are total differentials (with allowance made for that the integral  $\int \varphi(z)[d^3\varphi(z)/dz^3]dz$  is taken part by part) and that is why it is amenable to integration. In so doing one should bear in mind that  $\tilde{\mu}_e(f) - \mu_e^0(f) = RT\ln\{\theta_R^0/[1-\theta_R^0]\} + RTa_0\theta_R^0 - F\varphi^0$  and  $\tilde{\mu}_m(f) - \mu_m^0(f) = RT\ln C_m^0 + z_m F\varphi^0$ , where the superscript "0" marks bulk values of the variables. Subsequent solution should be performed, probably, numerically. Probably, it could in part be conducted by the boundary-layer method, for (17) contains small parameter  $(\lambda^2 a_0/Cc)$  at the higher derivative. This work will be performed later on. As to here and now, we will point to a simpler continuation. In particular, we will presume that the addend with the second derivative in the equation for the electrochemical potential of electrons is irrelevant. Then integral (17) will give the link between the squared field  $[d\varphi(z)/dz]^2$  and concentrations  $C_m$  and  $C_R$ . The results that would be obtained as a result of this manipulation could then be used either for the construction of a solution of a more total integral (17) (with allowance made for the addend  $(RT\lambda^2 a_0/Cc)d^2 C_R(z)/dz^2$  by the boundary-layer method) or as a first approximation for the corresponding numerical solution.

#### 4. Effects of Short-Range Interactions

To within a first approximation (i.e. under the assumption about the inessentialness of the differential addend in the expression for the electrochemical potential of electrons), the integral of the system of equations for surface layers is probably easier to find by using a differential way for writing down such equations:

$$\begin{aligned} & [1/(1-\theta_R)]dC_R/dz - C_R d(F\varphi/RT)/dz \\ & + a_0 C_R d\theta_R/dz = 0, \\ & dC_m/dz + z_m C_m d(F\varphi/RT)/dz = 0, \quad (18) \\ & d^2\varphi(z)/dz^2 = -(4\pi F/\varepsilon_f)[z_0 C + z_m C_m - C_R]. \end{aligned}$$

Upon taking the sum of the first two equations and taking into account the third equation, we will have

$$\begin{aligned} & dC_m/dz + [1/(1-\theta_R)]dC_R/dz \\ & - (\varepsilon_f/4\pi RT)d^2\varphi(z)/dz^2 d\varphi/dz \\ & - (Fz_0 C/RT)d\varphi/dz + a_0 C_R d\theta_R/dz = 0. \end{aligned}$$

After integrating this equation, we obtain

$$\begin{aligned} & [d\varphi/dz]^2 = (8\pi RT/\varepsilon_f)\{C_m - C_m^0 \\ & - C\ln[(1-\theta_R)/(1-\theta_R^0)] + (Ca_0/2)[\theta_R^2 - (\theta_R^0)^2] \\ & - (Fz_0 C/RT)[\varphi - \varphi^0]\}. \quad (19) \end{aligned}$$

The last addend in the braces in the right-hand part of (19) can be expressed through the degree of occupation  $\theta_R$ , bearing in mind that for the last from the first equation of system (18) there follows the relationship

$$\begin{aligned} & \theta_R/(1-\theta_R) = [\theta_R^0/(1-\theta_R^0)] \\ & \times \exp[-a_0(\theta_R - \theta_R^0)] \exp\{F[\varphi - \varphi^0]/RT\}. \quad (20) \end{aligned}$$

Having expressed  $F[\varphi - \varphi^0]/RT$  therefrom, after substitution into (19), we will have

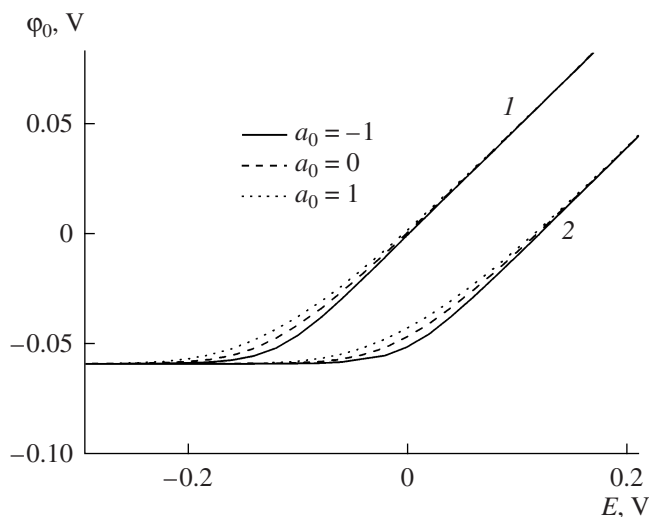
$$\begin{aligned} & [d\varphi/dz]^2 = (8\pi RT/\varepsilon_f)\{C_m - C_m^0 \\ & - C\ln[(1-\theta_R)/(1-\theta_R^0)] + (Ca_0/2)[\theta_R^2 - (\theta_R^0)^2] \\ & + z_0 C\ln[\theta_R^0(1-\theta_R)/\theta_R(1-\theta_R^0)] - \\ & - a_0 z_0 C[\theta_R - \theta_R^0]\}. \quad (21) \end{aligned}$$

This leads to the equations

$$\begin{aligned} & [d\varphi/dz]^2 = (8\pi RT/\varepsilon_f)\{C_m - C_m^0 \\ & - C\ln[(1-\theta_R)/(1-\theta_R^0)] + (Ca_0/2)[\theta_R^2 - (\theta_R^0)^2]\} \\ & z_0 = 0, \quad z_m = 1, \end{aligned} \quad (21a)$$

$$\begin{aligned} & [d\varphi/dz]^2 = (8\pi RT/\varepsilon_f)\{C_m - C_m^0 \\ & - C\ln[\theta_R/\theta_R^0] + (Ca_0/2)[(1-\theta_R)^2 - (1-\theta_R^0)^2]\} \\ & z_0 = 1, \quad z_m = -1, \end{aligned} \quad (21b)$$

for the special cases of the chargednesses of redox fragments  $z_0 = 0$  and  $z_m = 1$  that had previously been considered in paper [3]. The conclusion that suggests itself from a comparison of these relationships is that the passing from the first case ( $z_0 = 0, z_m = 1$ ) to the second case ( $z_0 = 1, z_m = -1$ ) is likely to correspond to the substitution of  $(1-\theta_R)$  and  $(1-\theta_R^0)$  for  $\theta_R$  and  $\theta_R^0$ , respectively. A more detailed formulation for the rule of such a transition may be obtained with allowance made for the expressions describing the degrees of occupation by the reduced form,  $\theta_R$ , and by the oxidized form,  $(1-\theta_R)$ , which represent an alternative to equation (20)



**Fig. 1.** Equilibrium potential  $\phi^0$  of the film bulk as a function of the electrode potential: (1)  $k_m = 0.1$ ,  $k_e = 0.1$  and (2)  $k_m = 0.1$ ,  $k_e = 10$ ; all the curves were calculated for  $z_m = 1$  and  $C = C_0 = C_s = 1$  M.

and which are valid the particular value of  $z_0$  notwithstanding:

$$\begin{aligned} \theta_R &= k_e \exp[-a_0 \theta_R] \exp(F[\phi - E]/RT) / \{1 \\ &+ k_e \exp[-a_0 \theta_R] \exp(F[\phi - E]/RT)\} \\ (1 - \theta_R) &= \{1 + k_e \exp[-a_0 \theta_R] \\ &\times \exp(F[\phi - E]/RT)\}^{-1}, \end{aligned} \quad (20a)$$

where  $k_e = \sigma'_e / \rho'_e$  is a coefficient that refers to the distribution of electrons between the substrate and the film. Marking parameters and variables in the first of these equations with the superscript “(0)” and ascribing the superscript “(1)” to the same quantities in the second equation, i.e. presuming that the values of the quantities thus singled out correspond to values  $z_0 = 0$  and  $z_0 = 1$ , respectively, we can equate these equations to one another:

$$k_e^{(0)} \exp[-a_0^{(0)} \theta_R^{(0)}] \exp(F[\phi^{(0)} - E^{(0)}]/RT) / \{1 + k_e^{(0)} \exp[-a_0^{(0)} \theta_R^{(0)}] \exp(F[\phi^{(0)} - E^{(0)}]/RT)\} \quad (22)$$

$= 1 / \{1 + k_e^{(1)} \exp[-a_0^{(1)} \theta_R^{(1)}] \exp(F[\phi^{(1)} - E^{(1)}]/RT)\}$ . Using this device is equivalent to the presumed rule of transition from  $z_0 = 0$  to  $z_0 = 1$ , i.e. to the substitution of  $(1 - \theta_R)$  for  $\theta_R$  and allows us to establish correspondence now between potentials  $\phi^{(0)}$  and  $\phi^{(1)}$ ,  $E^{(0)}$  and  $E^{(1)}$ , as well as between parameters  $a_0^{(0)}$  and  $a_0^{(1)}$ ,  $k_e^{(0)}$  and  $k_e^{(1)}$ . Complementing relationship (22) by the requirement that, in the course of the same transition, values of concentrations of counterions coincide with one another ( $C_m^{(0)} = C_m^{(1)}$ ), i.e.

$$k_m^{(0)} C_0 \exp[-F\phi^{(0)}/RT] = k_m^{(1)} C_0 \exp[F\phi^{(1)}/RT], \quad (23)$$

where  $k_m$  is a coefficient that takes into account the distribution of ions between the film and solution, we can easily obtain conditions for the correspondence of results realized in the said instances of values of  $z_0$ :

$$a_0^{(0)} = a_0^{(1)} = a_0; \quad k_m^{(0)} = k_m^{(1)}; \quad (24)$$

$$k_e^{(1)} = \exp[a_0]/k_e^{(0)}; \quad \phi^{(0)} = -\phi^{(1)}; \quad E^{(0)} = -E^{(1)}.$$

In other words, as in the case of  $a_0 = 0$  (see [3]), the results of an analysis conducted at  $z_0 = 0$  can be viewed valid for  $z_0 = 1$  by altering in the relationships to be obtained the sign of potentials and the coefficient of distribution of electrons  $k_e^{(0)}$  to  $k_e^{(1)} = \exp[a_0]/k_e^{(0)}$ . The discovered correspondence allows us to restrict our subsequent consideration merely by the case where  $z_0 = 0$ .

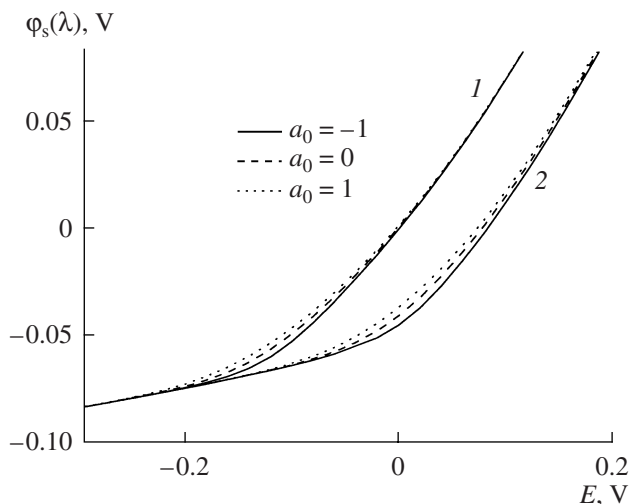
The goal of our further analysis is to establish how the exchange currents of injection of charge carriers into a film depend on the electrode potential  $E$  and the concentration of the washing electrolyte  $C_s$  in a first approximation with respect to the effect of the short-range interactions. When trying to find a solution for this problem for the structure of EDL at the substrate/film and film/solution interfaces below, as in [3, 11], there will be used models of Stern and Gouy, respectively. As it will be demonstrated somewhat later, such a problem reduces to the determination of dependences of the potential of the thickness of a film,  $\phi^0 = f_1(E, C_s)$ ; the potential of the first layer of the film that is adjacent to the substrate,  $\phi_s(\lambda) = f_2(E, C_s)$ ; and the potential of the last layer of the lattice (i.e.  $M$ th),  $\phi_s(L)$  as a function of the same variables. The equation that defines the potential value in the thickness of the film at  $z_0 = 0$  is the condition of local electroneutrality:  $C_m^0 = C_R^0 = C\theta_R^0$ , which, with allowance made for the bond of  $C_m^0$  with the concentration of counterions in electrolyte  $C_0$  and potential  $\phi^0$  (see for example [23]), leads to the following expression:

$$\phi^0 = (RT/F) \ln[k_m C_0 / C\theta_R^0]. \quad (25)$$

On the other hand, from the expression for  $\theta_R^0$  we presented in the foregoing, it is easy to establish with the aid of (25) that the electrode potential  $E$  is connected with this degree of occupation and with parameters of the system through the equation

$$E = (RT/F) \ln \{k_e k_m C_0 (1 - \theta_R^0) / C[\theta_R^0]^2\} - RT a_0 \theta_R^0 / F. \quad (26)$$

Ascribing some value or another to the attraction constant  $a_0$  in (25) and (26) and specifying a series of values of  $\theta_R^0$  out of the interval (0, 1), we can find potentials  $\phi^0$  and  $E$  that correspond to them. This allows us to find a family of dependences  $\phi^0(E, a_0)$ . The results of the corresponding calculations are presented in Fig. 1 (see the caption to this figure).



**Fig. 2.** Equilibrium potential  $\varphi_s(\lambda)$  of the first layer of the lattice adjacent to the substrate as a function of the electrode potential: (1)  $k_m = 0.1$ ,  $k_e = 0.1$  and (2)  $k_m = 0.1$ ,  $k_e = 10$ ; all the curves were calculated for  $z_m = 1$  and  $C = C_0 = C_s = 1$  M; the lattice constant  $\lambda$  is equal to  $10^{-7}$  cm,  $\varepsilon_s = 10\varepsilon_f = 80\varepsilon_0$ , where  $\varepsilon_0 = 0.354\pi \times 10^{-10}$ .

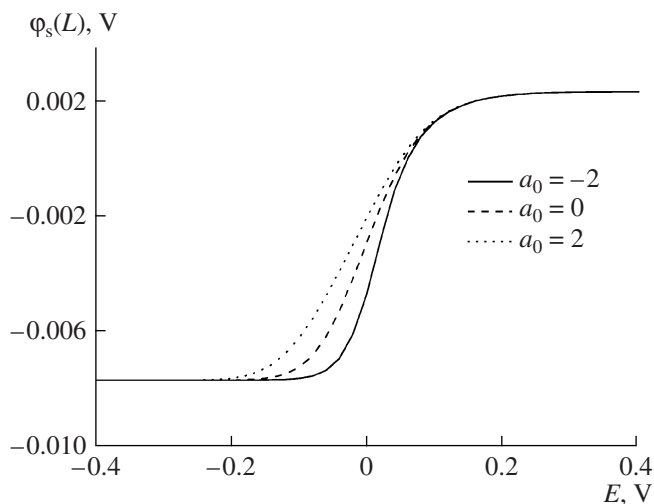
Presuming that the Stern model is valid for the EDL structure at the substrate/film interface and the Gouy model holds true for the film/solution interface, the conditions for the continuity of the induction vector at these two interfaces can be written in the following form:

$$\begin{aligned} \varepsilon_\lambda d\varphi/dz|_{z=\lambda-0} &= \varepsilon_f d\varphi/dz|_{z=\lambda+0}; \\ \varepsilon_f d\varphi/dz|_{z=L-0} &= \varepsilon_s d\varphi/dz|_{z=L+0}, \end{aligned} \quad (27)$$

i.e. in the form that presumes the absence of any charge adsorbed at the interfaces  $z = \lambda$  and  $z = L$ , where, again,  $L$  is the thickness of the film and parameter  $\varepsilon_\lambda$  is the dielectric constant of the first layer of the lattice, which will be set in what follows equal to  $\varepsilon_f$ . An explicit form of writing for the first of these conditions is the equation

$$\begin{aligned} [\varphi_s(\lambda) - E]^2 &= (8\pi RT\lambda^2/\varepsilon_f)\{C_m(\lambda) - C_m^0 \\ &- C \ln[(1 - \theta_R(\lambda))/(1 - \theta_R^0)] \\ &+ (Ca_0/2)[\theta_R^2(\lambda) - (\theta_R^0)^2]\}. \end{aligned} \quad (28)$$

Here, by the quantities  $\varphi_s(\lambda)$ ,  $C_m(\lambda)$ , and  $\theta_R(\lambda)$  we understand values of the variables in the first plane of a polymer lattice (an analogue of the Helmholtz plane in the Stern model) that is adjacent to the substrate. It should also be pointed out that relationship (28) takes into account the expression for the derivative  $d\varphi/dz|_{z=\lambda+0}$ , which follows from (21a). In so doing, the derivative  $d\varphi/dz|_{z=\lambda-0}$  was presumed, as usual, equal to  $[\varphi_s(\lambda) - E]/\lambda$ . As the links of concentrations  $C_m(\lambda)$  and  $\theta_R(\lambda)$  with potentials  $\varphi_s(\lambda)$  and  $E$  are known (see for example (22) and (23)), and as the dependence  $\varphi^0(E, a_0)$  was determined by the technique described in the foregoing, then, (28), when solved together with (20a), allows us to compute the corresponding values of potential  $\varphi_s(\lambda)$ .



**Fig. 3.** Equilibrium potential  $\varphi_s(L)$  at the film/solution interface as a function of the electrode potential, calculated at  $k_m = 0.1$ ,  $k_e = 1$ ,  $C = C_0 = C_s = 1$  M,  $z_m = 1$ ,  $\varepsilon_s = 10\varepsilon_f = 80\varepsilon_0$ ,  $\lambda = 10^{-7}$  cm.

The results of such computations, which were carried out for the collection of parameters that was applied for the construction of Fig. 1, are presented in Fig. 2.

As is known, in the case of a washing solution of a symmetrical 1.1-electrolyte of the concentration  $C_s$  and dielectric constant  $\varepsilon_s$ , the field's square is given by the equation

$$[d\varphi/dz]^2 = (8\pi RTC_s/\varepsilon_s)\{\exp[-F\varphi/2RT] - \exp[F\varphi/2RT]\}^2, \quad z \geq L. \quad (29)$$

That is why the second condition in conditions (27) will be written in the form

$$\begin{aligned} \{\exp[-F\varphi_s(L)/2RT] - \exp[F\varphi_s(L)/2RT]\}^2 \\ = (\varepsilon_f/\varepsilon_s C_s)\{C_m(L) - C_m^0 \\ - C \ln[1 - \theta_R(L)/(1 - \theta_R^0)] \\ + (Ca_0/2)[\theta_R^2(L) - (\theta_R^0)^2]\}. \end{aligned} \quad (30)$$

Here,  $\varphi_s(L)$  is the potential of the film surface bordering the electrolyte that washes it, whereas  $C_m(L)$  and  $\theta_R(L)$  are the near-surface (on the side of the film) concentrations of counterions (in the case of under consideration, cations) and the degree of occupation by the reduced form, respectively. It is obvious that with the aid of (30) we can conduct calculation of the surface potential  $\varphi_s(L)$ . The results of such calculations are presented in Fig. 3 in the form of dependences of  $\varphi_s(L)$  as a function of the electrode potential  $E$ . In this case the electrolyte concentration  $C_s$  was set equal to  $C_0$ , as is frequently the case in conditions of experiment.



As we have already mentioned in the foregoing, knowledge about potentials  $\varphi^0$ ,  $\varphi_s(\lambda)$ , and  $\varphi_s(L)$  allows us to calculate dependences of exchange current densities for electrons  $I_{im}^0$  and counterions  $I_m^0$  on the electrode potential  $E$  and the concentration  $C_0$ . Preliminarily it is necessary to point out that the following expression is valid for the rate of injection of electrons  $I_{im}(0) = -Fj(0)$  in a first approximation with respect to allowance for the effect of the short-range interactions:

$$I_{im}(0) = -F\{\sigma'_e[1 - \theta_R(\lambda)]\exp[-\alpha_1 a_0 \theta_R(\lambda)] \times \exp[-(\alpha_1 F/RT)(E - \varphi_s(\lambda))] - \rho'_e \theta_R(\lambda) \times \exp[\beta_1 a_0 \theta_R(\lambda)] \exp[(\beta_1 F/RT)(E - \varphi_s(\lambda))]\}. \quad (31)$$

It is easy to be convinced that this relationship follows from (15) after the expulsion of  $\theta_R^0$  from (15), providing we take into consideration the substitution of  $\theta_R(\lambda)$  for  $\theta_R(1)$  in the notation we used for the degree of occupation of the first layer of the lattice, which was conducted in this section and which is connected with the transition to a local description. We can also add that, previously, (31) was introduced in review [11] without any detailed justification. After performing linearization of (31) with respect to small deviations  $\delta\theta_R(\lambda)$ ,  $\delta E$ , and  $\delta\varphi_s(\lambda)$  (and, subsequently, with respect to  $\delta\theta_R^0$  and  $\delta\varphi^0$  as well) from certain initial (equilibrium) values, we can establish the following expression:

$$I_{im}(0) = -I_{im}^0 \Lambda_0 \delta C_R^0 / C_R^{(0)} (1 - \theta_R^{(0)}) - (I_{im}^0 F/RT) \delta[E - \varphi^0]. \quad (32)$$

Here,  $\Lambda_0 = 1 + a_0 \theta_R^0 (1 - \theta_R^{(0)})$ ,  $I_{im}^0$  is the density of the exchange current of the process of injection of electrons, for which, obviously, valid are the expressions

$$I_{im}^0 = -F\sigma'_e[1 - \theta_R^{(0)}(\lambda)]\exp[-\alpha_1 a_0 \theta_R^{(0)}(\lambda)] \times \exp[-(\alpha_1 F/RT)(E^{(0)} - \varphi_s^{(0)}(\lambda))] \quad (33) \\ = -F\rho'_e \theta_R^{(0)}(\lambda)\exp[\beta_1 a_0 \theta_R^{(0)}(\lambda)] \times \exp[(\beta_1 F/RT)(E^{(0)} - \varphi_s^{(0)}(\lambda))],$$

where the superscript “(0)” marks initial values of the variables.

Identical, though somewhat different, forms of relationships (33) may be obtained by passing from  $\theta_R^{(0)}(\lambda)$  and  $\varphi_s^{(0)}(\lambda)$  to values of the variables in the thickness of the film ( $\theta_R^0$  and  $\varphi^0$ , respectively); such relationships were presented in [11] and, as was the case with equations (32) and (33), in the absence of the forces of the short-range interactions (i.e. in the case of  $a_0 = 0$ ), these coincide with those that were used in work [3].

For the rate of injection of counterions into a film (i.e. at  $z = L$ ), as was done in works [3, 11], we can use the equation

$$I_m(L) = z_m F \{ \sigma_m C_0 \exp[-z_m F \varphi_s(L)/RT] - \rho_m C_m^0 \exp[z_m F (\varphi^0 - \varphi_s(L))/RT] \}, \quad (34)$$

whose linearization with respect to small deviations  $\delta C_m^0$ ,  $\delta\varphi_s(L)$ , and  $\delta\varphi^0$  from the initial values of these variables gives

$$I_m(L) = -(I_m^0 / C_m^{(0)}) \delta C_m^0 - (F I_m^0 / RT) \delta[E - \varphi^0]. \quad (35)$$

The density of the exchange current by counterions  $I_m^0$  that appears here is given by the relationships

$$I_m^0 = z_m F \sigma_m C_0 \exp[-z_m F \varphi_s^{(0)}(L)/RT] \quad (36) \\ = z_m F \rho_m C_m^{(0)} \exp[z_m F (\varphi^{(0)} - \varphi_s^{(0)}(L))/RT],$$

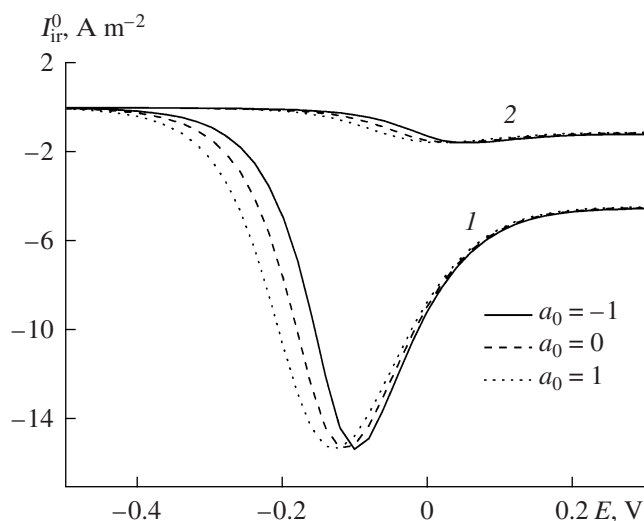
where, as in the foregoing, the superscript “(0)” marks the initial values of the variables. In the writing of equation (34) it was presumed that, firstly, the structure of EDL at the film/solution interface may be described in terms of the Gouy model (see [3, 11]) and, secondly, that the limiting stage of the injection of counterions into the film is localized directly on the physical boundary between the film and the solution ( $z = L$ ). The emergence of such a limiting stage should, more likely than not, be attributed to the occurrence of partial desolvation of ions in that process.

The results of calculations of exchange current densities for electrons  $I_{im}^0$  and counterions  $I_m^0$  as functions of the electrode potential  $E$  are presented in Figs. 4 and 5, respectively. Values of constants  $\sigma'_e$  and  $\sigma_m$  in the calculations were selected so as to ensure the equality of these currents to within an order of magnitude (see captions to the figures).

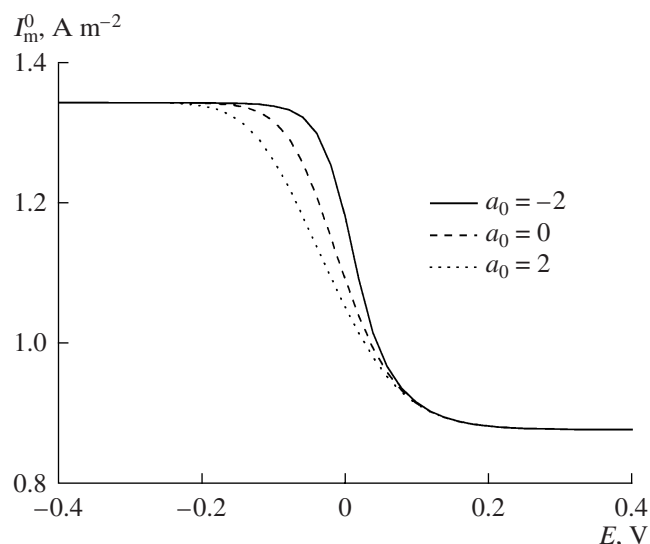
#### IV. DISCUSSION OF THE RESULTS

Restricting, for the time being, our consideration to the part of the results that are illustrated by the figures we presented, we deem it possible to state that the effect of the short-range interactions is substantial even in a first approximation. At the same time, its influence is not considerable enough to lead to qualitative alterations in the distribution of potential in the film (here, potentials  $\varphi^0$ ,  $\varphi_s(\lambda)$ ,  $\varphi_s(L)$ ) and exchange currents as compared with the role of the zeroth approximation (i.e. at  $a_0 = 0$ ). Such qualitative alterations should be expected to commence only in the case of large negative values of  $a_0$ , for which parameter  $\Lambda_0 = 1 + a_0 \theta_R^{(0)} (1 - \theta_R^{(0)})$  may happen to be negative. However, as is well known, the molecular-field approximation that was used in the foregoing happens to be incorrect in this case (see for example [7]).

From the figures presented in this paper it follows that a noticeable difference between the results of the zeroth and first approximations takes place solely for



**Fig. 4.** Density of exchange current of electrons  $I_{ir}^0$  as a function of the electrode potential: (1)  $k_m = 0.1$ ,  $k_e = 0.1$ ,  $C = C_0 = C_s = 1$  M and (2)  $k_m = 0.1$ ,  $k_e = 10$ ,  $C = C_0 = C_s = 1$  M; all the curves were calculated for  $z_m = 1$ ,  $\epsilon_s = 10\epsilon_f = 80\epsilon_0$ ,  $\lambda = 10^{-7}$  cm,  $\sigma'_e = 10^{-4}$  mol m $^{-2}$  s $^{-1}$ .



**Fig. 5.** Density of exchange current of counterions  $I_m^0$  as a function of the electrode potential, calculated at  $k_m = 0.1$ ,  $k_e = 1$ ,  $C = C_0 = C_s = 1$  M,  $z_m = 1$ ,  $\epsilon_s = 10\epsilon_f = 80\epsilon_0$ ,  $\lambda = 10^{-7}$  cm,  $\sigma_m = 10^{-7}$  mol m $^{-2}$  s $^{-1}$ .

some intermediate values of the electrode potentials  $E$ . In this intermediate zone of potentials, the calculated parameters (in particular, exchange currents) do not yet reach values that correspond to the extremely high positive or negative values of the electrode potential  $E$ . As in the case of cyclic voltammograms, the transition from a zero value of parameter  $a_0$  to a negative value of this parameter leads to the narrowing of the interval of potentials where basic alterations in the calculated parameters occur; conversely, the transition to positive values of parameter  $a_0$  leads to its expansion. We deem it possible to presume with much assurance that the alterations that are discovered for the exchange currents are likely to be observed also in the case of interfacial capacitances. Calculations of such capacitances in a zeroth approximation were performed in [3] and may apparently be performed in the first approximation under consideration as well. Mentioning these results in the particular communication does not seem worthwhile, for it is connected with the generalization of quite a number of definitions given in work [3]. The description of a method for obtaining corresponding data, as well as the results of allowance for the forces of the short-range interactions in a second approximation, will be performed separately.

## V. CONCLUSIONS

Briefly considering on the whole the analysis performed in this work, it should be noted that it can be generalized at the expense of using a more complicated model (allowance for the deformation constituent, the presence of the solvent, and so on). In the framework of

the same approach it would be possible to consider the kinetics of the growth of an electroactive film or poly-layered adsorption and some other heterogeneous processes.

## VI. ACKNOWLEDGMENTS

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